ACID MINE DRAINAGE TREATMENT WITH OPEN LIMESTONE CHANNELS¹

by

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Abstract. Acid mine drainage (AMD) is often associated with mining of pyritic coal and metal deposits. Typical AMD associated with coal mines in the eastern U.S. can have acidity and iron concentrations ranging from the teens to the thousands of mg/l. Aluminum and manganese can be present in concentrations ranging from zero to the low hundreds of mg/l. Much attention has been devoted to developing inexpensive, limestone (LS)-based systems for treating AMD with little or no maintenance. However, LS tends to coat with metal hydroxides when exposed to AMD in an oxidized state, a process known as "armoring". It is generally assumed that once armored, LS ceases to neutralize acid. Another problem is that the hydroxides tend to settle into plug the pore spaces in LS beds forcing water to move around rather than through the LS. While both are caused by the precipitation of metal hydroxides, armoring and plugging are two different problems. Plugging of LS pores can be avoided by maintaining a high flushing rate through the LS bed. Armoring, however, occurs regardless of water velocity. This study investigated the influence of armoring on LS solubility and the implications of armoring and plugging on the construction of open (oxidizing) LS channels for treating AMD. We evaluated the AMD treatment performance of armored and unarmored LS in oxidizing environments both in laboratory and field studies. The results showed ferric and aluminum hydroxide floc remained suspended in solution until the LS was allowed to dry. As the floc dried, the LS became armored. The laboratory study treated AMD with armored LS (ALS) from two field sites and unarmored LS (ULS). ALS dissolved 25 to 33% more slowly than ULS. The field study surveyed 2- to 8-year-old rock-lined waterways constructed for erosion control. One waterway was constructed of sandstone rip-rap and seven others were constructed with LS. The results indicated that OLC's, though armored, continued to reduce acidity at rates similar to those of the laboratory study. The results were used to verify a dissolution kinetics model which predicts the required dimensions of an OLC for treatment of given flows and acidities.

Additional Key Words: Abandoned mine lands, chemical water treatment, passive treatment, reclamation

Introduction

Acid mine drainage (AMD) continues to be one of the largest problems facing the mining industry. AMD originates from active and abandoned mines as pyrite (FeS₂) or other metal sulfides associated with the mineral deposit are exposed to oxidizing conditions. Upon exposure, the sulfide minerals progress through a combination of auto-oxidation and microbial oxidation reactions to produce large amounts of acid, iron and sulfate. This acidity then dissolves other minerals,

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releasing ions such as manganese and aluminum. The resulting solution is AMD. Upon reaching a stream, AMD alters the chemical balance: it consumes alkalinity, introduces metal ions and generally degrades its biological productivity. If sufficiently severe, AMD will also render the receiving waters unfit for human, agricultural, industrial or recreational use (Atlas and Bartha 1987).

AMD can be treated with alkali chemicals and this is the method of choice for most active mines. This is expensive and must continue long after mining has ceased. An alternative is passive treatment. Passive treatment refers to any zero to low maintenance AMD treatment scheme. These systems are of increasing interest as state, industry and federal partnerships are formed to rehabilitate watersheds damaged by historic mining. Passive systems offer low maintenance, inexpensive, and long-term solutions to AMD remediation (Brodie 1990, Hedin 1989). Anoxic limestone drains (ALDs), wetlands, or a combination of both are the most often used passive systems (Faulkner and Skousen 1994). Wetlands are effective in-handling low acid loadings but often encounter difficulties or fail under high loading. Problems with ALDs occur when ferric iron, aluminum,

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or ferrous iron and dissolved oxygen are present. Under these conditions, metals will precipitate and armor the LS reducing its dissolution efficiency compared to unarmored LS. Precipitates may occlude all of the pore volume within the drain preventing water from contacting the LS.

Studies by Pearson and McDonnell (1974, 1975a, 1975b) found that armored LS (ALS) dissolved at about 20% the rate of unarmored LS (ULS). Ziemkiewicz et al. (1994) conducted a preliminary study of OLCs on field sites and developed a spreadsheet to estimate LS volumes and channel dimensions for treating AMD. Open limestone channels will become armored, presumably reducing the limestone dissolution rate to 20% of ULS. But unlike ALDs, plugging of LS pores can be controlled by maintaining high flows and the armoring effect can be accounted for by adding a design factor of five (Ziemkiewicz et al. 1994).

This study compares the AMD treatment efficiency of armored and unarmored LS in the laboratory. In addition, a field study was conducted to survey existing open LS-lined waterways to evaluate the effects of armored LS on AMD treatment.

Experimental Design

Laboratory Study

The lab study was conducted using containers high-density liter. polyethylene) filled with 2.3 kg (5 lbs) of 5 - 10 cm (2 - 4 in) ALS or ULS (Figure 1). One of five sources of AMD or deionized water (blank) (1.2 liters) was added to each of the containers. The two sources of ALS were from Robinson Run (RR) and Dola, WV. The ULS was from the Deer Valley formation provided by



Action Mining in Somerset County, PA. The five AMD sources (all Pittsburgh coal bed) were: Maidsville Seep near Morgantown, WV; Shaw Mines Run and Weir-11, near Meyersdale, PA; Coal Run, near Salisbury, PA; and a synthetic AMD containing only sulfuric acid and deionized water. Only 13 of the 18 possible LS/water combinations were used in the study (Table 1), and each of the selected combinations had 3 replications.

The method for estimating the solubility of ALS vs. ULS was adapted from Watzlaf and Hedin (1993).

Water samples (60 mls) were collected with 60-ml plastic syringes from containers in duplicate (one sample for general water chemistry and one for metals analysis) at the following time intervals after water introduction: 0 hr, 1 hr, 2 hrs, 4 hrs, 6 hrs, 12 hrs, 18 hrs, and 24 hrs. The samples were filtered (0.45 micron) and metal analyses samples were acidified with 1 ml of concentrated nitric acid prior to submission to the NRCCE Analytical Laboratory for analysis. The parameters tested were: pH (electrode), electrical conductivity (conductivity bridge), alkalinity and acidity (Brinkman auto-titrator), and concentrations of iron, aluminum, manganese, calcium, magnesium (Leaman Labs inductively coupled plasma spectrometry), and sulfate (Milton Roy Spectronic 20) (Clesceri et al. 1989).

Field Study

The field study surveyed existing rock-lined waterways on abandoned mine lands (AML) sites containing AMD (Table 2). These waterways were constructed for erosion control or stream bank stabilization only. One waterway was constructed with sandstone and the other seven waterways were made with LS. Two water samples (250 mls each) were collected at identified distances along the channels (one for general water chemistry and one for metals analysis) and analyzed as described above (Clesceri et al. 1989). The samples were field filtered (0.45 micron) and acidified with 1 ml of nitric acid for metals analysis or cooled to 4°C for general chemistry. Flows were measured with a Marsh -McBirney model 2000 Flo-Mate electromagnetic flow meter for larger flows (> 95 l/min or 25 gpm) or a calibrated bucket and a stopwatch for smaller flows (<95 l/min or 25 gpm). Distances were measured with a 100foot surveying rope.

The results of water quality analyses from field channels were plotted against our kinetics spreadsheet (RBOLD) designed to predict the dimensions required to treat AMD with OLCs (Ziemkiewicz et al. 1994). RBOLD translates ALS dissolution kinetics into spreadsheet which estimates the reduction in acid load for a given LS channel, or estimates the size of a channel required to achieve desired acid load reductions.

Description of Field Sites

NRCS Coral/Graceton Site

The Coral/Graceton site is located adjacent to U.S. Route 119 immediately northeast of the towns of Coral and Graceton in Indiana County, PA. The channel is 220 m long, 3 m wide and 0.1 m deep (720 x

Table 1. Water and limestone combinations u	sed in the laboratory study.	Each combination
checked had three replications.		
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Water	Robinson Run ALS	Dola ALS	ULS
Maidsville	х		Х
Shaw Mines		x	Х
Weir-11		x	х
Coal Run		x	х
Synthetic AMD		х	Х
Deionized Water	X	x	х

 9×0.5 ft) on a 10% slope, and was constructed with sandstone. The flow of AMD through the channel, measured at the source and mouth of the rock lined waterway, was 1323 l/min (350 gpm) and the acidity at the source was 550 mg/l.

Morgantown Airport Site

The Morgantown Airport site is located adjacent to U.S. Routes 119/857 east of Morgantown, WV. There are two channels (both LS and heavily armored) at this location. The first channel (West) is 46 m long, 1.3 m wide and 0.1 m deep (150 x 4 x 0.5 ft) on a 14% slope. The second channel (East) is branched, with the first branch being 21 m long (70 ft) and the second branch being 27 m (90 ft) long (same widths and depth as West channel) both on 20% slopes. The flow of AMD in the West channel was 113 l/min (30 gpm) and the acidity was 410 mg/l. The total combined flow in the East channel was 76 l/min (20 gpm) and the acidities were 355 mg/l for the first branch and 335 mg/l in the second. The flow rates were equal at the sources and the mouths of each channel.

NRCS Eichleberger #2 Site

The Eichleberger #2 site is located in Bedford County, PA, 6.5 km southeast of the village of Coaldale. The channel is 49 m long, 2 m wide and 0.1 m deep (160 x 6 x 0.5 ft) on a 20% slope, and was constructed with LS that became heavily armored. The flow through the channel was consistent at 378 l/min (100 gpm) and the acidity at the source was 510 mg/l.

Pa DER Site

The Pennsylvania Dept. of Environmental Resources site is located in Bedford County, PA, 1.6 km west of the village of Defiance. This channel is 11 m long, 1 m wide, and 0.1 m deep $(37 \times 3 \times 0.5 \text{ ft})$ on a slope of 60% with a flow of 95 l/min (25 gpm). The acidity was 2600 mg/l at the source. This channel is also constructed of LS that became heavily armored.

PA Game Commission Site

The Pennsylvania Game Commission site is also a small channel of 11 m long, 1 m wide, and 0.1 m deep $(35 \times 3 \times 0.5 \text{ ft})$ on a slope of 45%. It is located on the northeast side of Vintondale in Cambria County, PA. The flow is 484 l/min (128 gpm) and the acidity is 330 mg/l at the source. This channel was constructed of LS and became armored after construction.

Cottage Town Site

The Cottage Town site is located 1.6 km west of Cairnbrook in Somerset County, PA. The channel is 137 m long, 1.3 m wide and 0.1 m deep ($450 \times 4 \times 0.5$ ft) on a 9% slope with a flow of 302 l/min (80 gpm) throughout the entire length. LS was used for the construction of the channel. The LS was heavily armored and the AMD had an acidity of 32 mg/l at the source.

NRCS - Opawsky Site

The Opawsky site is located in Armstrong County, PA, 1 km south of Mosgrove. This site was different from the other sites due to the construction of a wetland 46 m (150 ft) that was installed at the bottom of the upper section of OLC. The top portion of the channel was constructed of LS for 46 m long, 2 m wide and 0.3 m deep (150 x 6 x 2 ft) on a slope of 9%. The LS was armored and the flow of AMD throughout the entire system was 907 l/min (240 gpm). This portion of the channel entered a wetland that covered an area of 350 m² (7.6 m by 46 m). The lower 137 m (450 ft) of the channel was also constructed of LS that was armored. The acidity at the source was 30 mg/l.

<u>Results</u>

Laboratory Study

The initial acidity of the Maidsville seep (2080 mg/l) was reduced to 925 mg/l (56% reduction) after 24 hours with RR ALS (Figure 2). This compares to ULS that eliminated 65% of the acidity after 24 hours. The ALS from Dola completely eliminated the Shaw Mines'



initial acidity of 518 mg/l in the containers after 6 hrs (Figure 3). Unarmored LS achieved 100% treatment after 4 hrs. Alkalinity production leveled off after 12 hours for both armored (75 mg/l) and unarmored (120 mg/l) LS.



The initial acidity of Weir-11 (1370 mg/l) was reduced to 20 mg/l (99% reduction) after 21 hours using Dola ALS (Figure 4). Unarmored LS treated all the acidity and produced 50 mg/l alkalinity during the same time period. Coal Run, a stream contaminated by a turn of the century deep mine, had an initial acidity of 905 mg/l (Figure 5). The Dola ALS and ULS both completely neutralized the acidity of the water after 21 hrs. Both types of LS produced net alkaline water during the same time period, producing 61 mg/l for the Dola ALS and 84 mg/l for ULS.





Deionized water was added to the three LS types used in the study to isolate the effect of armoring in the absence of acid leachate. The results indicate that the ALS initially produced some acidity but that the solutions became alkaline within the first hour. The ULS produced the highest alkalinities at 50 mg/l while Dola ALS produced 30 mg/l and RR ALS gave 40 mg/l (Figure 6).

The three LS types were treated with a synthetic AMD (0.02M H_2SO_4). The acidity was completely neutralized within 2 hrs with ALS and within 1 hr for ULS. Alkalinity generation leveled off at 67 mg/l after 18 hrs for ALS and 85 mg/l after 4 hrs for ULS (Figure 7).



Figure 7. Acidity and alkalinity generation of Synthetic AMD with armored and unarmored limestone.

Four water types used in the study were placed in cells and monitored over a 14 hr period to confirm whether any changes occurred in acidity levels on exposure to air. Figure 8 indicates that no changes occurred.

Field Study

The NRCS Coral/Graceton waterway was constructed with sandstone to serve as a control to LS channels. The prediction line was based on the use of LS. The resulting acidity reduction on the site was 0.0028% per ft (Table 2), much less than the predicted 0.034% per ft if it would have been constructed with LS (Figure 9).



Figure 8. Acidity changes over time with three AMD sources without limestone.



The Morgantown Airport West channel performance was better than predicted (Figure 10). The actual acidity reduction was 0.0800% per ft (Table 2) compared to the predicted reduction of 0.032% per ft. The Morgantown Airport East channels also performed better than predicted with an acidity reduction of 0.0780% per ft compared to a predicted reduction of 0.020% per ft (Figure 11).

The NRCS Eichleberger #2 channel also performed better than expected with an actual acidity reduction of 0.2250% per ft compared to a predicted reduction of 0.104% per ft (Figure 12). The PA DER site is a very short channel with high acidity, but removes 0.1080% of the acidity per ft. This was an order of magnitude better than the predicted acidity reduction of 0.010% per ft (Figure 13).







Figure 11. Observed and predicted acidity reductions of an open limestone channel at the Morgantown Airport east drain.





Figure 13. Observed and predicted acidity reductions of an open limestone channel at the Pa DER site in Bedford County, PA.

The PA Game Commission OLC is also a very short channel (Figure 14), but it shows an impressive performance (1.7710% acidity removal per ft compared to a predicted performance of 0.044% per ft acidity removal). The steep grades of these two channels really increased water velocities and enhanced LS dissolution.





The Cottage Town site has a small amount of acidity entering the channel (Figure 15) and exhibits an acidity removal better than that predicted over the first 110 m (360 ft) of the channel (0.0870% per ft compared to 0.035% per ft predicted). Acidity increases over the last 27 m (90 ft) of the channel probably due to a small source of AMD entering at the base of the channel. But

this brings the overall acidity removal closer to the predicted value (.0290% compared to .0350% per ft of channel).







The NRCS Opawsky site's performance was slightly worse than predicted (0.33% acidity removal per ft compared to a predicted removal of 0.42% per ft) but still removed 50% of the acidity (Figure 16).

Discussion and Conclusions

In the laboratory study, ALS treated acidity onethird to one-fourth as fast as ULS. This factor also applies to alkalinity production from these two types of LS. These values are close to the one-fifth factor reported by Pearson and McDonnell (1974). Acidity reduction of OLCs in the field varied between 4% and 62%, and acid reductions per ft of channel were between .029 and 1.77% (Table 2). The steeper channels performed better than the two channels with shallower (9%) slopes. In the sandstone channel, acidity decreased by only 2% and by a factor of .0028% per ft of channel.

The results confirmed the logarithmic acidity decay curve with ALS reported by Pearson and McDonnell (1974). Thus acidity removal by ALS is proportional to the increment of channel length and cross sectional area, regardless of initial acidity. In other words, a fixed proportion of acidity is removed by ALS per ft of channel (width and depth included). Acidity loss is rapid at first then gradually slows down.

OLC's work best on steep slopes. The key factor in designing OLCs is to prevent iron and aluminum flocs from settling out and plugging the LS pores in the channel. One LS channel not reported here was found on a nearly flat slope (1 to 3%). It was filled with floc and was ineffective in treating acidity. The successful channels generally had slopes above 10% and used coarse LS (15-to 30-cm sized material or 6- to 12- in sized material). Both slope and size of LS can maximize void space and water velocity thereby inhibiting floc settling. Evidence of the effect of slope on ALS dissolution is seen on the PA Game Commission and PaDER sites that had LS channels constructed on slopes > 40%.

Each of the passive treatment systems (aerobic wetlands, anaerobic wetlands, ALDs, APS, and OLCs) have an area of application (see Faulkner and Skousen 1995 for descriptions and applications of each). It will be difficult to achieve effluent limits by passive water treatment in most cases by using any one method alone. However, coupling these systems could allow some acidity reduction and metal precipitation with one system, then routing the water into another system for additional acidity and metal removal. The primary application of most passive treatment systems will be on watershed restoration projects, AML sites, and perhaps for pretreatments for active treatment systems using chemicals. OLCs are particularly useful in steep terrain where long (300 to 1000 m) channels are possible, and they offer a unique treatment where no other passive system is likely to be appropriate. OLCs will produce metal flocs, so settlement basins should be incorporated in the design. Larger OLCs should have settling ponds or wetlands placed at intermediate points (flat channel segments) to remove the precipitates and help prevent plugging.

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Site	Flow	Length	type	Slope	Initial.	Final	Loss	Acid loss
	(gpm)	(ft)		(%)	(mg/l)		(%)	(%/ft)
Coral/Graceton	350	720	SS	10	550	540	2	.0028
Morg Airport E	20	90	LS	20	355	330	7	.0780
Morg Airport W	30	150	LS	14	410	360	12	.0800
Eichleberger #2	100	160	LS	20	510	325	36	.2250
Pa-DER	25	37	LS	60	2600	2500	4	.1080
PA Game Com.	128	35	LS	45	330	125	62	1.7710
Cottage Town	80	450	LS	9	32	28	13	.0290
Opawsky	240	150	LS	9	30	15	50	.3333

Table 2. Characteristics and performance of a sandstone open channel and eight OLCs at field sites in Pennsylvania and West Virginia (SS=sandstone, LS=limestone).

The age of the channels we studied varied from 2 to 8 yrs and none of these channels had required maintenance. If constructed correctly, OLCs should be nearly maintenance free and less expensive to construct than other AMD treatment systems.

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